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14. ABSTRACT We have acquired a gas chromatograph (GC) to investigate post-shock sampling of shock-heated hydrocarbon fuels. The GC has four analytical columns, which allow for the precise measurement of permanent gases (e.g. O2, N2, CO, CO2, CH4), clear separation (and therefore ppm-level measurement) of C2 and C3 hydrocarbons, and detection of aromatics and hydrocarbons C4 and larger. A sampling system has been implemented on one of our existing shock tube facilities and is used to extract a 14.6-cm3 sample of shock-heated gas, 2 cm from the shock tube and wall. GC analysis of the gas sample yields a measurement of the ultimate mole fraction values of species					
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## Report Title

Final Report: Fast-Sampling Gas Chromatography (GC) System for Speciation in a Shock Tube

### ABSTRACT

We have acquired a gas chromatograph (GC) to investigate post-shock sampling of shock-heated hydrocarbon fuels. The GC has four analytical columns, which allow for the precise measurement of permanent gases (e.g. O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>), clear separation (and therefore ppm-level measurement) of C<sub>2</sub> and C<sub>3</sub> hydrocarbons, and detection of aromatics and hydrocarbons C<sub>4</sub> and larger. A sampling system has been implemented on one of our existing shock tube facilities and is used to extract a 14.6-cm<sup>3</sup> sample of shock-heated gas, 2 cm from the shock tube end wall. GC analysis of the gas sample yields a measurement of the ultimate mole fraction values of species at the end of the reflected shock test time. Simultaneous in situ optical measurements allow for a comparison of the sampled and optically measured results. Initial experimental results show good agreement between optical measurements and GC analysis results for cold shock experiments, and both techniques capture similar ethylene decomposition rates for temperature-dependent shock experiments.

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Jesse Streicher	0.00	
FTE Equivalent:	0.00	
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Names of Post Doctorates

NAME	PERCENT SUPPORTED
FTE Equivalent:	
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Names of Faculty Supported

NAME	PERCENT SUPPORTED	National Academy Member
R. K. Hanson	0.00	Yes
FTE Equivalent:	0.00	
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Dr. David Davidson

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### Sub Contractors (DD882)

### Inventions (DD882)

### Scientific Progress

See attached report.

### Technology Transfer

We have discussed with Prof. Ken Brezinsky of University of Illinois at Chicago and Dr. Robert Tranter of Argonne National Laboratory (both who are strong proponents of single-pulse shock tube GC sampling) and Dr. Med Colket of UTRC (with experience in jet fuel GC analysis) about our novel application of simultaneous GC sampling and laser absorption in a shock tube.



# **Final Report**

## **Fast-Sampling Gas Chromatography (GC) System for Speciation in a Shock Tube**

August 1, 2015 through July 31, 2016  
Defense University Research Instrumentation Program (DURIP)

by

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Army Research Office  
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Dr. Ralph Anthenien Jr.

October 31, 2016

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## Abstract

We have acquired a gas chromatograph (GC) to investigate post-shock sampling of shock-heated hydrocarbon fuels. The GC has four analytical columns, which allow for the precise measurement of permanent gases (e.g. O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>), clear separation (and therefore ppm-level measurement) of C<sub>2</sub> and C<sub>3</sub> hydrocarbons, and detection of aromatics and hydrocarbons C<sub>4</sub> and larger. A sampling system has been implemented on one of our existing shock tube facilities and is used to extract a 14.6-cm<sup>3</sup> sample of shock-heated gas, 2 cm from the shock tube end wall. GC analysis of the gas sample yields a measurement of the ultimate mole fraction values of species at the end of the reflected shock test time. Simultaneous *in situ* optical measurements allow for a comparison of the sampled and optically measured results. Initial experimental results show good agreement between optical measurements and GC analysis results for cold shock experiments, and both techniques capture similar ethylene decomposition rates for temperature-dependent shock experiments.

## Problem Statement

Stanford's recent work on a fast-kinetics scheme to model the pyrolysis reactions that dominate the first phase of hydrocarbon oxidation relies on the ability to measure key hydrocarbon fragments (e.g. ethylene, methane, and acetylene) over a wide range of temperatures and pressures. The optical diagnostics developed at Stanford for measuring the time-resolved formation of these key species are crucial to this endeavor, but the addition of an extractive, sampling-based measurement technique allows for the measurement of species not yet measureable by optical methods (e.g. H<sub>2</sub>, benzene). Additionally, simultaneous laser- and sampling-based measurements provide the opportunity for a direct comparison of the two measurement techniques.

## Gas Chromatograph (GC) Sampling System Overview

We have acquired a 4-column GC (Agilent 490 MicroGC) for analysis of post-shock gas samples. Each of the four columns (MolSieve 5Å, PoraPLOT U, PoraPLOT Q, CP-Sil 5 CB) targets a specific kind of species or subset of hydrocarbons. A fast-acting solenoid valve (Festo MHE3) is mounted on the Stanford Aerosol Shock Tube (AST) 2 cm from the shock tube end wall via a custom-made sidewall plug (see Figure 1a) below). The Festo valve has a nominal flow rate of 200 L/min and can open and close in approximately 5 msec. A 1/4-inch diameter, 33-inch long, stainless steel tube is attached to the sampling valve and serves as the containment vessel for the extracted gas sample (total volume of 14.6 mL). The GC extracts a sample from the sampling line volume via a 1/16-inch diameter, 7.5-inch long, Sulfinert-treated, stainless steel tube. All of the tubing that makes up the sampling system is maintained at 65 °C during experiments; the sample line segments are heated via resistance heating wire or tape heaters and wrapped with woven fiberglass insulation (see Figure 1b)). A schematic of the sampling system is shown in Figure 2.



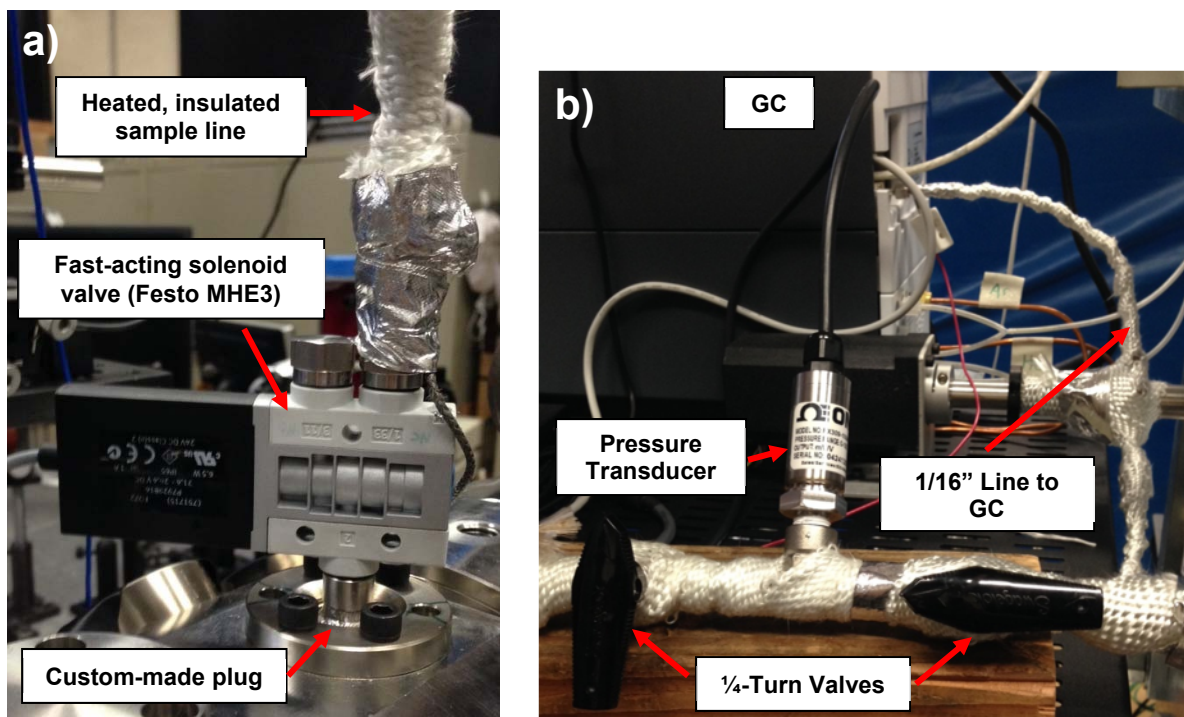


Figure 1: a) Fast-acting solenoid valve mounted on shock tube; b) Section of heated, insulated sample line, including 1/16" line leading to GC

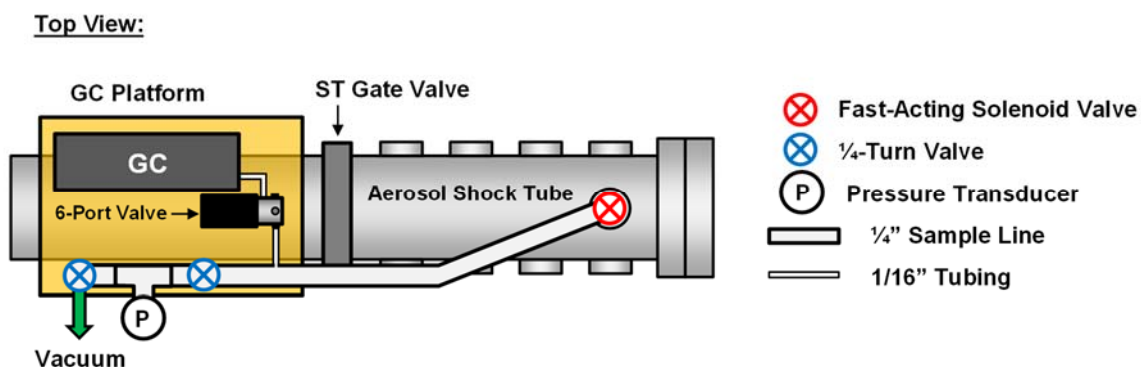


Figure 2: Schematic of AST GC sampling system (top view)

Before running a shock experiment, the fast-acting valve is closed and the sample line is evacuated. When a shock experiment is conducted, the 1/4-turn valve leading to vacuum is closed, thereby isolating the evacuated sample line. The sampling event is initiated when the fast-acting valve is triggered by the arrival of the reflected shock wave 2 cm from the end wall; the valve opens 10 msec after the reflected shock wave arrives and remains open for 0.8 sec.

Within 2 sec of the completion of the sampling event, the second 1/4-turn valve (upstream of the vacuum valve and pressure transducer) is closed, thereby trapping the first 2.2 mL of gas to enter the sample line. This volume is primarily made up of unreacted test gas that resides in the dead volume present in the sidewall plug (see Figure 3). During each shock experiment, this volume

remains unshocked and therefore retains the initial test gas composition. The volume of test gas residing in the plug is approximately 0.63 mL – much less than the isolated gas volume (2.2 mL).

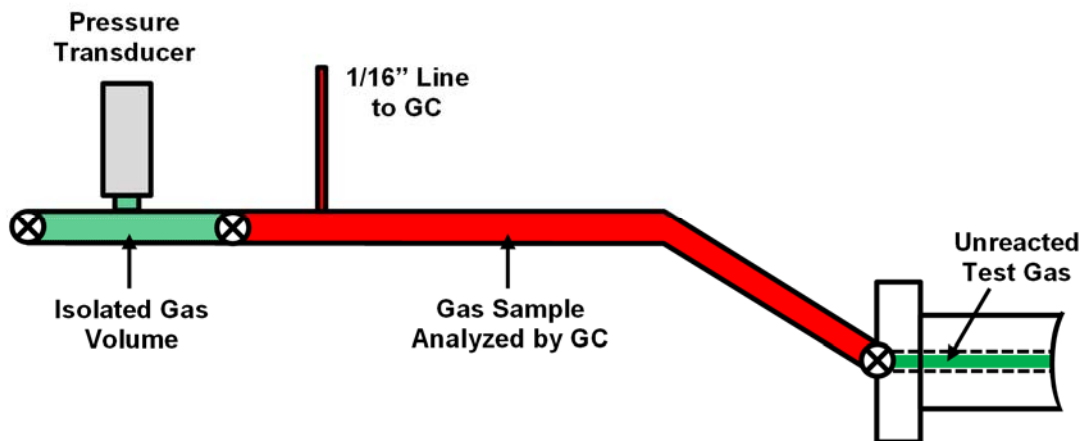


Figure 3: Schematic of sampling system unreacted gas volume and isolated volume

Two samples are extracted from the sample line and analyzed by the GC for each shock experiment. The analysis of the second sample is taken to be the final GC measurement, as the first sample is susceptible to dilution by residual argon in the GC (used to flush out the GC between each experiment) and trace amounts of unreacted test gas.

## GC Sampling System Validation Experiments

A series of experiments was conducted to validate the sampling system procedure and results. A 0.2% ethylene/balance argon fuel mixture was shock-heated to ~6 atm and ~1000 K – a temperature low enough that no thermal decomposition would occur. As can be seen in Table 1, GC analysis of post-shock gas samples from five “cold” shock experiments shows **99.8% recovery of the initial ethylene** at these conditions. This indicates a 5 ppm loss of ethylene, on average, between the source gas mixture and the recovered sample analyzed by the GC. These results suggest that at these conditions, negligible dilution occurs and the composition of the sample extracted from the shock tube is statistically identical to the composition of the gas at the core of the shock tube.

Table 1: Cold shock results: GC- and laser-measured ethylene mole fractions (T5 ~1000 K, P5 = 6.0-6.3 atm). Nominal, initial ethylene mole fraction is 0.2%.

Shock Number	T5	GC-Measured C <sub>2</sub> H <sub>4</sub> Mole Fraction (%)	Laser-Measured C <sub>2</sub> H <sub>4</sub> Mole Fraction (%)
1	1050 K	0.1998	0.2007
2	1015 K	0.1993	0.2025
3	990 K	0.1995	0.1903
4	1055 K	0.1993	0.2032
5	1060 K	0.1996	0.2004
Average:			
		0.1995	0.1994

A CO<sub>2</sub> gas laser (10.532 micron emission line) was used to simultaneously record time-resolved ethylene mole fraction for these low-temperature shock experiments (see Table 1). Similar to the GC measurements, the optical measurements show **99.7% ethylene retention** between initial fuel loading and post-shock conditions when measured at the end of the test time (approximately 1.5-2 msec after the arrival of the reflected shock wave).

## Ethylene Pyrolysis Experiments: GC and Laser Measurements

*In situ* optical and sampled-gas results were recorded for a similar fuel mixture (1.0% ethylene/argon) over a range of temperatures (1200-2000 K) at ~5 atm. The GC was used to measure the ultimate mole fraction value of four species (ethylene, methane, acetylene, and hydrogen) at each shock condition. With the GC sampling system in its current configuration (i.e., sampling for 0.8 seconds, starting 10 msec after the arrival of the reflected shock wave 2 cm from the shock tube end wall), the GC measurements cannot be directly compared to the laser-based measurements. However, in tandem, the laser and GC results can provide valuable insight into the efficacy and accuracy of published chemical kinetic models.

Figure 4 shows a comparison of the ultimate ethylene mole fractions measured using the GC and those predicted using the USC Mech v2 kinetic mechanism<sup>1</sup>. Overall, the two datasets trend similarly with temperature and closely agree at temperatures below 1300 K and above 1800 K. However, the kinetic mechanism underpredicts the decomposition of ethylene between 1300 and 1800 K.

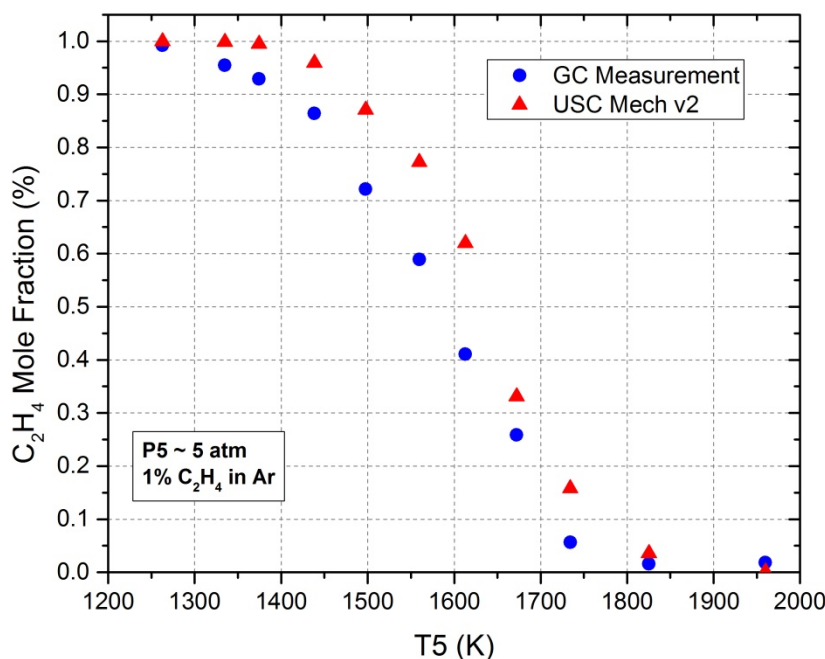


Figure 4: Ultimate ethylene mole fraction - GC measurement vs. USC Mech v2 (1% C<sub>2</sub>H<sub>4</sub>/Ar, P5 ~5 atm)

<sup>1</sup> Hai Wang, Xiaoqing You, Ameya V. Joshi, Scott G. Davis, Alexander Laskin, Fokion Egolfopoulos & Chung K. Law, USC Mech Version II. High-Temperature Combustion Reaction Model of H<sub>2</sub>/CO/C<sub>1</sub>-C<sub>4</sub> Compounds. [http://ignis.usc.edu/USC\\_Mech\\_II.htm](http://ignis.usc.edu/USC_Mech_II.htm), May 2007.

The underprediction of ethylene decomposition by the USC mechanism is further confirmed by the measurement of three additional species using the GC, as well as laser measurements. Figure 5a) shows a comparison of the ultimate values of mechanism-predicted and GC-measured ethylene, acetylene, hydrogen, and methane. Figure 5b) shows the percent carbon recovered by the GC measurements, relative to the amount of initial carbon in the system (i.e. 1%  $C_2H_4$ ).

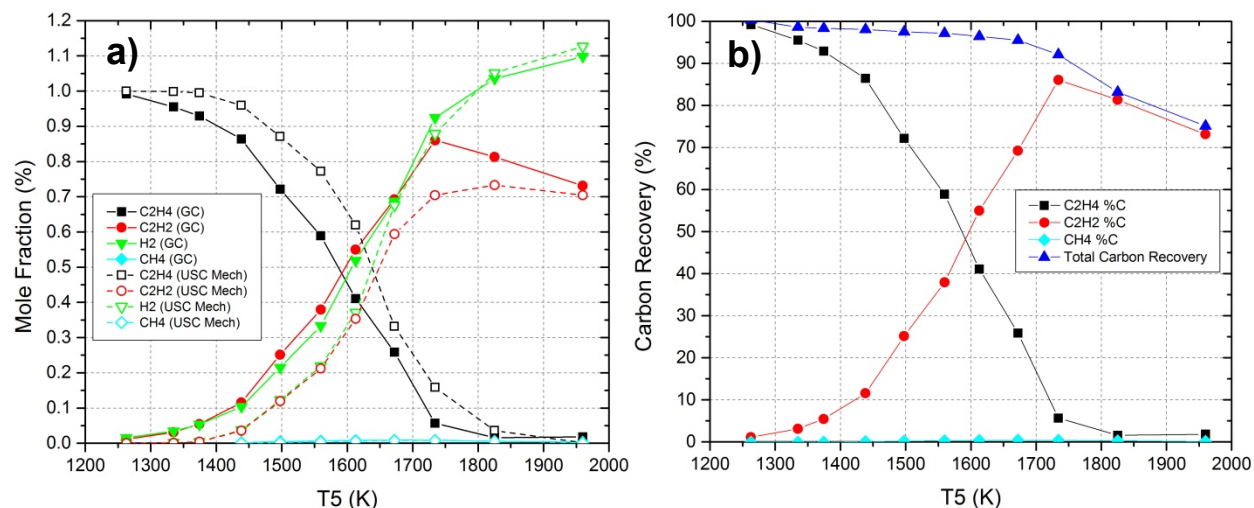
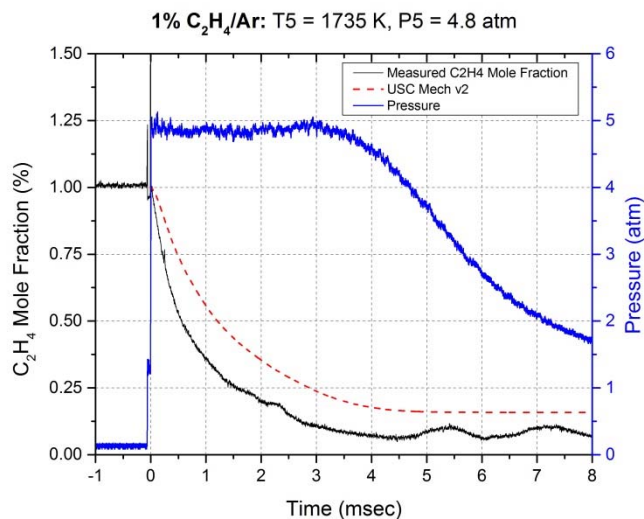


Figure 5: a) Ultimate ethylene, methane, acetylene mole fraction comparison (GC vs. USC Mech v2); b) Carbon recovery analysis based on GC measurements

Figure 5a) confirms that even at temperatures where the USC mechanism would suggest negligible ethylene decomposition (1300-1400 K), the GC measurements indicate non-negligible acetylene and hydrogen yields. Also, the carbon recovery analysis of the GC results (Figure 5b)) shows >97% carbon recovery at these temperatures; this high carbon recovery percentage indicates that the decrease in ethylene yield between 1300 and 1400 K is not an artifact of measurement uncertainty, but a true indicator of ethylene pyrolysis at these low temperatures. (It should be noted that the drop in carbon recovery seen above 1700 K is due to the formation of diacetylene,  $C_4H_2$ , at high temperatures (an indicator of acetylene thermal decomposition). Diacetylene was not measured in these experiments.)

Even at higher temperatures (1400-2000 K), it can be seen that the USC mechanism continues to underpredict the decomposition of ethylene, and therefore also underpredicts the formation of acetylene and hydrogen. This trend is further confirmed by time-resolved laser measurements of ethylene mole fraction. Figure 6 shows laser-measured ethylene mole fraction as a function of time compared with the time-resolved kinetic mechanism prediction of ethylene mole fraction. Pressure measured 2 cm from the shock tube end wall is also plotted for reference.



**Figure 6: Time-resolved ethylene mole fraction comparison (laser measurement vs. USC Mech v2)**

The slope of the laser measurement in Figure 6 clearly shows that ethylene breaks down at a much faster rate than what is predicted by the USC mechanism. This result is consistent with the observation that the mechanism predicts higher ultimate ethylene yields than what is recovered in the GC measurements.

When used together, the ethylene laser diagnostic and GC sampling system form a powerful tool that enables us to better understand the thermal decomposition of various hydrocarbons and fine-tune chemical kinetic mechanisms. In the case of the ethylene decomposition experiments presented here, the measured ethylene laser traces will be used to optimize the reaction rate parameters in the USC mechanism so that the ethylene decay prediction will more closely match the measured decay rate.

## Future Work

The GC measurements taken thus far using the post-shock sampling system are very promising – temperature-dependent trends can be captured by analyzing post-shock gas samples and both GC and laser measurements suggest further work is needed to optimize one chemical kinetic mechanism in particular – USC Mech v2. The successes in studying the pyrolysis of ethylene – a relatively simple, small hydrocarbon fuel – indicate that the sampling system can now be used to study larger, more complex hydrocarbon fuels with confidence. The GC sampling system will next be used to study n-heptane pyrolysis, followed by first-stage n-heptane ignition. Ultimately, the sampling system will be used to study the pyrolysis and oxidation of real fuels, including JP-8 and diesel. As the complexity of the studied fuels evolves, so too will the diagnostics used to study them. The suite of species analyzed using the GC will be expanded and additional optical diagnostics will be implemented for comparison. Finally, the sampling system will be modified to obtain multiple samples per shock experiment, thereby providing time-resolved species data that could be directly compared to laser results.